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Molecular Interactions and Properties with Many-Body Methods

AFOSR-90-0079

to

Air Force Office of Scientific Research

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I. Introduction

A variety of Air Force applications require highly detailed information about atoms, molecules, and their interactions. This information is necessary in problems ranging from chemical laser development, to the detection and identification of rocket plumes, to non-linear optics, electron beam technology, and high density and energy fuels.

The crucial component needed to understand molecular reactions is the potential energy surfaces (PES) that serve to describe the attractions among the atoms and molecules. However, such information is not easy to obtain. In many cases, the most direct approach to obtaining accurate potential surfaces for molecules, and detailed information about their excited states, vibrational spectra, and a wealth of other quantities, is high level *ab initio* solutions of the Schrödinger equation.

However, more so than in most other areas, the ability to provide reliable quantum mechanical results for increasingly large molecules depends critically on improved method development. Whereas supercomputers can enable us to make much larger computations with old methods, the simultaneous development of new methods can increase computational capability by further orders of magnitude. In this regard, many-body perturbation theory (MBPT) and its infinite-order extensions termed coupled-cluster (CC) methods offer a number of attractive features that the more traditional configuration interaction approaches lack.

Under AFOSR support, we have established these CC/MBPT theories as being among the most accurate available, and have developed very efficient and generally applicable computer programs to perform CC/MBPT calculations. Also, we have employed these methods for the first time in large-scale *ab initio* calculations of potential energy surfaces. The successes of our original work in this effort have been substantial (see previous AFOSR reports).

Following a statement of research objectives, we review the recent scientific advances we have made under AFOSR support.

II. Research Objectives

The overall objective of our continuing research program for AFOSR has included the following:

1. The development of new, more accurate and more efficient *ab initio* quantum mechanical methods based upon coupled-cluster (CC) and many-body perturbation theory (MBPT) for determining molecular properties and potential energy surfaces for molecular interactions.
2. The implementation of these methods into highly efficient, transportable computer programs (ACES II), to enable computations on molecules to be made on an almost routine basis, for a wide variety of different properties.
3. The application of these techniques to a variety of problems that are of interest to AFOSR, and that serve to establish the range of accuracy for CC/MBPT methods.

The underlying goal of our effort is highly accurate first principle quantum mechanical predictions of molecular properties. Such tools are already making possible the determination of dissociation energies, moments, polarizabilities, excitation energies, and vibrational and

rotational spectra for molecules to an accuracy that is predictive and comparable to experiment. Furthermore, for transient molecules as occur in rocket plumes, combustion, flame chemistry, and interstellar space that are generally difficult to study experimentally, theoretical calculations will provide otherwise inaccessible information. In addition, theoretical work provides the underlying framework to understand innumerable important molecular phenomena and to suggest previously unanticipated solutions to defense related problems. All of the new methods which we develop are being incorporated into our Advanced Concepts in Electronic Structure II (ACES II) program system. The program has been established at Air Force installations for use by other Air Force researchers.

III. Notable Accomplishments This Past Year

- A. In a major achievement, we presented the first results from the full CCSDT method for open shell molecules^{2,*}. Comparison with full CI demonstrated exceptional agreement. We also employed several different open-shell references, including unrestricted Hartree Fock (UHF), restricted open-shell Hartree Fock (ROHF), and quasi-restricted Hartree Fock (QRHF). This study complements our presentation of CCSDT for closed shells in 1987.
- B. Our next major contribution was to present an algorithm for the convenient inclusion of Abelian symmetry into CC calculations.⁴ This "Direct Product Decomposition Approach" provides an enormous improvement in computational speed. All steps after the molecular integrals can potentially gain by a factor of h^2 where h is the order of the symmetry group. For a D_{2h} molecule, this means a CC calculation can be done up to 64 times faster than without symmetry. By also recognizing that we can represent all the products in the highly non-linear CC equations exclusively in terms of recursively computed intermediates, we are able to perform CC calculations solely in terms of generalized matrix products. These features are incorporated into our entirely rewritten ACES II program with the net result that we can do correlated calculations from about 2 to 100 times faster than other popular program packages like GAUSSIAN 90.
- C. The ozone (O_3) molecule has proven to be a highly demanding test case for the most powerful quantum mechanical methods. Usually reliable methods give a very wrong ordering of the vibrational frequencies, with some even implying that O_3 would not have C_{2v} symmetry, e.g. Since O_3 is much too large for a full CI result, we provided a benchmark CCSDT result.⁶ Unlike *all* methods that had a less complete inclusion of triple excitations like MBPT(4), CCSDT-1, CCSD+T(CCSD), etc. and multi-reference CI, CCSDT provides the most accurate results for O_3 frequencies compared to experiment. This application is also the largest CCSDT calculation ever reported.
- D. We also addressed the fascinating question of whether NO_3 is D_{3h} (i.e. has all N-O bond lengths equal) as all textbooks would assume, or is a distorted C_{2v} structure (with one N-O bond different than the others). This problem poses great difficulties for quantum mechanical calculations, because a slight displacement of the molecule from the point where

* References in this section refer to the publications listed under: Publications Supported by AFOSR (1990 — 1991), pg. 6.

the molecule is D_{3h} to C_{2v} gives a discontinuity in the energy for most applicable methods.⁵ The reason is that the open-shell UHF or ROHF solution at D_{3h} symmetry does not have D_{3h} symmetry (i.e. “symmetry breaks”). This kind of symmetry breaking permeates many molecular and solid state applications, and even though the exact solution shows no such symmetry breaking, any correlation method short of full CI cannot resolve the difficulty. Our solution to the problem is only made possible in CC theory. The CCSD wavefunction is $\exp(T_2)\exp(T_1)\Phi_0$, and the $\exp(T_1)$ operator has great ability to rotate the orbitals forming the single determinant reference function Φ_0 to be whatever they need to be to describe the relevant physics. This enables us to take orbitals from NO_3^- , which is a closed shell, and whose wavefunction, unlike that for NO_3 , smoothly connects as the D_{3h} anion is distorted to the C_{2v} form. By simply deleting an electron from the highest orbital occupied in NO_3^- , we obtain what we have called a quasi-restricted Hartree Fock (QRHF) reference. Like an ROHF, the QRHF reference is an eigenfunction of spin, but unlike the ROHF, it does not suffer from symmetry breaking. At the CCSD level, the C_{2v} form is very slightly lower in energy than is the D_{3h} , although the inclusion of triple excitation reverses the slight difference to be in favor of the D_{3h} form. Excitation energies for the lowest lying states are in excellent agreement with recent experimental data, although the experiments remain inconclusive on the definitive structure.

- E. As shown above for O_3 , of great practical importance are the effective inclusion of higher excitations like T_3 excitations on top of CCSD methods. For sufficiently difficult examples, even T_4 will become important. The computational dependence of such terms can be up to n^{10} (n is the size of basis set) times the number of iterations for CCSDTQ and n^8 for CCSDT. Furthermore, compared to n^6 for CCSD, their proliferation is such that often the only viable techniques for their inclusion lies in non-iterative methods. We introduced a method called CCSD+TQ*(CCSD) that puts in the initial T_3 and T_4 contributions as a single evaluation of an n^8 quantity. All T_4 terms are included with only a single n^7 iteration, while the contribution of T_3 requires a single n^8 procedure. We have presented the first such methods that are correct through fifth order that include the T_4 and T_3 term.¹ Comparisons with full CI demonstrate their high accuracy. This is also demonstrated for the quasidegenerate H_4 system⁷ which poses a particular challenge for single reference CC methods. However, CCSD+TQ*(CCSD) performs exceedingly well even for this demanding case.
- F. In a notable advance⁸ involving open-shell gradients, we report such analytical derivative methods for the QRHF-CCSD method as described above for NO_3 . The method is illustrated by application to the methyl radical, CH_3 and the $^2\text{B}_2$ state of the NO_2 radical. This implementation is incorporated into ACES II showing the same exceptional speed as in the energy calculations themselves. All such methods are built upon the “relaxed density” concept we introduced some years back.
- G. In another paper on this subject¹⁰, we have further generalized our CCSD analytical derivative methods to include restricted open-shell Hartree-Fock (ROHF) references. This permits the treatment of open-shell molecules when spin contamination of an unrestricted Hartree-Fock (UHF) is a problem. Unlike the QRHF method where orbitals are taken from a different molecular state (NO_2^- for NO_2 , e.g.), the ROHF solution is the energetically

optimum choice, that is still *an eigenfunction of spin*. This, too, has its range of applications.

H. Finally, symmetry breaking for the potential curve where $F_2^+ \rightarrow F+F^+$ was considered.¹¹ This is a classic example where at R_e , $D_{\infty h}$ symmetry applies, but at $R \rightarrow \infty$, $C_{\infty v}$ applies. At the CC level with triples, we found that several different reference functions, symmetry broken or not, could be used with equal facility.

All of the above are important, timely developments in the field that provide solutions to molecular problems that in many cases, could not be previously addressed.

IV. Publications Supported by AFOSR (1990-1991)

1. R.J. Bartlett, J.D. Watts, S.A. Kucharski and J. Noga, "Non-Iterative Fifth-Order Triple and Quadruple Excitation Energy Corrections in Correlated Methods," *Chem. Phys. Lett.* **165**, 513 (1990).
2. J.D. Watts and R.J. Bartlett, "The Coupled-Cluster Single, Double and Triple Excitation Model for Open-Shell Single Reference Functions," *J. Chem. Phys.* **93**, 6104 (1990).
3. H. Sekino and R.J. Bartlett, Relativistic Coupled-Cluster Calculations on Neutral and Highly Ionized Atoms," *Int. J. Quantum Chem.* **S24**, 241 (1990).
4. J.F. Stanton, J. Gauss, J.D. Watts and R.J. Bartlett, "A Direct Product Decomposition Approach for Symmetry Exploitation in Many-Body Methods. I. Energy Calculations," *J. Chem. Phys.* **94**, 4334 (1991).
5. J.F. Stanton, J. Gauss and R.J. Bartlett, "Potential Nonrigidity of the NO_3 Radical," *J. Chem. Phys.* **94**, 4084 (1991).
6. J.D. Watts, J.F. Stanton and R.J. Bartlett, "A Benchmark Coupled-Cluster Single, Double and Triple Excitation (CCSDT) Study of the Structure and Harmonic Vibrational Frequencies of the Ozone Molecule," *Chem. Phys. Lett.* **178**, 471 (1991).
7. S.A. Kucharski, A. Balkova and R.J. Bartlett, "Performance of Single-Reference Coupled-Cluster Methods For Quasidegenerate Problems: The H_4 Model," *Theor. Chimica Acta* **80**, 321 (1991).
8. J. Gauss, J.F. Stanton and R.J. Bartlett, "Analytic Evaluation of Energy Gradients at the Coupled-Cluster Singles and Doubles Level Using Quasi-RHF Open-Shell Reference Functions," *J. Chem. Phys.* **95**, 2639 (1991).
9. S.A. Kucharski and R.J. Bartlett, "Recursive Intermediate Factorization and Complete Computational Linearization of the Coupled-Cluster Single, Double, Triple and Quadruple Excitation Equations," *Theor. Chimica Acta* **80**, 387 (1991).
10. J. Gauss, W.J. Lauderdale, J.F. Stanton, J.D. Watts and R.J. Bartlett, "Analytic Energy Gradients for Open-Shell Coupled-Cluster Singles and Doubles (CCSD) Calculations Using Restricted-Open-Shell-Hartree-Fock (ROHF) Reference Functions," *Chem. Phys. Lett.* **182**, 207 (1991).
11. J.D. Watts and R.J. Bartlett, "A Coupled-Cluster Study of Inversion Symmetry Breaking in The F_2^+ Molecular Ion," *J. Chem. Phys.* **95**, 6652 (1991).
12. J.F. Stanton, J. Gauss and R.J. Bartlett, "On the Choice of Orbitals for Symmetry Breaking Problems with Application to NO_3 ," *J. Chem. Phys.*, in press.

V. Invited Presentations (1990-1991)

June 1990 AFOSR Non-Linear Optical Polymers Contractors Meeting, Washington, DC
June 1990 W.N. Lipscomb 70th Birthday Symposium, Cambridge, MA

July 1990 Seventh American Conference on Theoretical Chemistry, San Diego, CA
July 1990 Seventy-Third Canadian Chemical Conference, Halifax, NS
Aug. 1990 Workshop on Coupled-Cluster Theory at the Interface of Atomic Physics and Quantum Chemistry, Cambridge, MA, organizer and speaker.
May 1991 American Chemical Society Joint Central-Great Lakes Regional Meeting, Indianapolis, IN
June 1991 Workshop on Recent Developments in Electronic Structure Algorithms, Ithaca, NY.
Aug 1991 Fourth Chemical Congress of North America, New York City, NY, organizer of symposium on *Ab Initio* Quantum Chemistry with Experiment.

VI. Students Supported (and Graduated)

Capt. Walt Lauderdale, Ph.D., December, 1991

David Bernholdt

Renee Mattie

Sullivan Beck

VII. Honors

Elected a fellow of the International Academy of Quantum Molecular Sciences, Menton, France, 1991. Only 30 members younger than 65 are allowed, and 65 members total.